A STUDY OF THE SOLUBILITY OF AROMATIC HYDROCARBONS IN WATER

BY

ROBERT LYNN BOHON

B.S., University of Illinois, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Introduction

Reliable data on the solubility of aromatic hydrocarbons in water is almost non-existent in the literature, and the temperature coefficient of these solubilities is not usually reported. The primary purpose of this research was to examine such solubilities and their temperature coefficients, and if possible interpret the results in terms of water structure and solubility mechanisms.

Procedure

The method of investigation consisted of saturating samples of air-free water at different temperatures with various aromatic hydrocarbons. The samples were then each subjected to analysis in a Beckman Ultraviolet Spectrophotometer, Model DU, previously set at the wavelength of maximum absorption for the compound in question. The absolute solubilities were then calculated from Beer's Law, the extinction coefficients having been determined in 95% ethanol solution. Except for *o*-xylene, which was believed to be impure, the values for solubility were believed accurate to within about one percent.

Benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, naphthalene and diphenyl were studied in pure water, and toluene was also studied in 0.400 molar silver nitrate solution.

The method used for the silver nitrate solutions was essentially that outlined by L. J. Andrews and R. M. Keefer (1) except that *n*-heptane was used as a solvent and a magnetic stirrer was utilized to ensure complete extraction of the hydrocarbon into the heptane layer.

Results

Table 1 presents a comparison of the solubilities determined in this study with those of reference (1). Concentration is expressed in grams per liter of saturated solution, and m/p represents the solubility in moles per liter corrected to the same vapor pressure in mm. of mercury for all the compounds. The last column is the molar volume in ml. per mole.

When compared at the same vapor pressure, the solubilities of the benzene hydrocarbons decrease as the molar volumes increase with the exception of *m*-xylene, which is about 6% more soluble than one would expect. The solubilities of naphthalene and diphenyl under these same conditions are seven to ten times as soluble as are the benzene hydrocarbons.

TABLE 1
Solubilities at 25°C

Compound	Concentration		(m/p) 10^4	V_M (liquids)
	Exp.	Lit.		
Benzene	1.79	1.74	2.41	89.401
Toluene	0.627	0.53	2.39	106.846
o-Xylene	(0.287)	0.204	(4.08)	121.193
Ethylbenzene	0.208	——	2.06	123.064
m-Xylene	0.196	0.173	2.22	123.456
p-Xylene	0.198	0.200	2.12	123.919
Naphthalene	0.0344	0.0315	25.0	133.2
Diphenyl	7.48×10^{-3}	5.94×10^{-3}	16.0	155.5
Toulene in .40m $AgNO_3$	1.09	——	4.14	——

The logarithm of the solubility was plotted versus the reciprocal of the absolute temperature for each system studied. A minimum occurred in the solubility curves for benzene, toluene, *m*-xylene, *p*-xylene, ethylbenzene, and probably *o*-xylene. This corresponds to a zero heat of solution which is generally associated with an "ideal" solution. The minimum occurs in every case at the same temperature, about 18°C.

This same phenomenon has been observed for the chloroethanes at about 20°C (2).

The heats of solution for these same liquid hydrocarbons appear to be very similar throughout the entire forty degree temperature range studied. They all have negative values of about 1 kcal. near 0°C, zero heats near 18°C, and positive heats of about 1.4 to 2.1 kcal. near 35°C.

The heats of solution for naphthalene and diphenyl when corrected for the heat of fusion (i.e., considered as supercooled liquids) are always positive; they never exhibit a zero heat of solution.

The change in heat of solution with temperature for the benzene hydrocarbons is about 100 calories per degree, and that for aliphatic hydrocarbons about 50 to 60 calories per degree. This temperature coefficient is also about 100 calories per degree for naphthalene, but it rises to almost 250 calories per degree for diphenyl. The heat of solution of diphenyl is about one kcal. higher than that for naphthalene.

A pure "volume entropy", ΔS_V, calculated from the solubilities and the equation (3)

$$\Delta S_V = R \ln V_W/V_M$$

is of the order of 12 to 16 entropy units for the benzene hydrocarbons and 20 to 25 for naphthalene and diphenyl. V_W is the volume of solution containing one mole of hydrocarbon, and V_M is the molar volume of the pure hydrocarbon. The difference between this value and the observed entropies of solution, $\Delta\overline{S}_{sol}$, was arbitrarily called the "entropy of freezing" and termed ΔS_W. Dividing ΔS_W by -5.26 e.u., the entropy of freezing to ice-I, gave the number of water molecules, N, which would "freeze" in order to give the observed entropy of solution. These values for N decreased linearly from about four at 0°C to two at 40°C.

Several possible mechanisms of solution are suggested to explain the data, but none appear to be completely satisfact-

ory. The most promising at present is a combination of two or more mechanisms acting against one another, one with a positive heat of reaction and the other with a negative heat of reaction.

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VITA

The author was born on July 20, 1925 in Decatur, Illinois. He attended the public schools in that city until 1943, when he graduated with honors from high school. After one semester and a summer term at James Millikin University in Decatur, the author enrolled in the college of Liberal Arts and Sciences at the University of Illinois as a chemical engineering major. Throughout most of his undergraduate training he was employed part-time as a chemist by the Anderson Physical Laboratories of Champaign. One summer was spent as a gas analyst at the Houdaille-Hershey Division of the Manhatten Project. The degree of Bachelor of Science with honors was awarded him in September, 1946.

In February, 1947 he entered the Graduate College of the University of Illinois and was employed as a special research assistant under contract with the United States Public Health Servile.

The author is a member of Alpha Chi Sigma, Sigma Xi, Sigma Tau, Phi Lambda Upsilon, Alpha Kappa Lambda, and the American Chemical Society.

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